# Unipolar supercurrent through graphene grafted with Pt-porphyrins: signature of gate-tunable magnetism.

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Inducing magnetism in graphene holds great promises, such as new exotic magnetic phases, or the control of exchange interaction via a gate electrode [1]. To reach this goals, graphene has been coated with magnetic or rare earth atoms [2, 3] as well as molecular magnets [4], with mixed results. Adsorbed magnetic atoms reduced graphene's mobility, with no concurrent magnetic signature. In contrast, the magnetisation reversal of molecular magnets could be detected in a graphene nanoconstriction. In the present work, we use Pt-porphyrins that interact with graphene's delocalised $sp^2$ orbitals. Neutral Pt-porphyrins are non magnetic, but the ionised form carries a magnetic moment of one Bohr magneton [5]. At room temperature we find that the molecules electron-dope the graphene, demonstrating that electron transfer occurs. More surprisingly, the grafted graphene's mobility increases. At low temperature, we show how superconducting contact electrodes can uniquely reveal the magnetic order induced in a mesoscopic, one-micron-long graphene sheet. The unipolar nature of the induced supercurrent, which is enhanced at negative gate voltage but suppressed at positive gate voltage, may be evidence for the long sought after Fermi-level controlled exchange interaction between localised spins and graphene.

The graphene sample was fully characterised before Pt-porphyrins grafting [6]. The pristine sample, with no porphyrins, displayed a bipolar superconducting proximity effect at low temperature. This means that at low enough temperature and high enough doping a supercurrent ran through the graphene. This supercurrent is termed bipolar because it occurs for both signs of gate voltage, corresponding to both electron and hole doping [7]. The fact that a supercurrent is induced through graphene, which is not itself a superconductor, means that phase coherence extends throughout the micron long graphene sheet (at low enough temperature), and that no magnetic flux threads the sample (to within one flux quantum).

The Pt-porphyrin molecules were deposited after warming the pristine sample back to room temperature. The room temperature effect of grafting is displayed in Fig. 1. We first notice the shift of the average Dirac peak position from $V_g = +10$ V (hole doping) to $V_g = -0.5$ V (Fig. 1b), demonstrating that
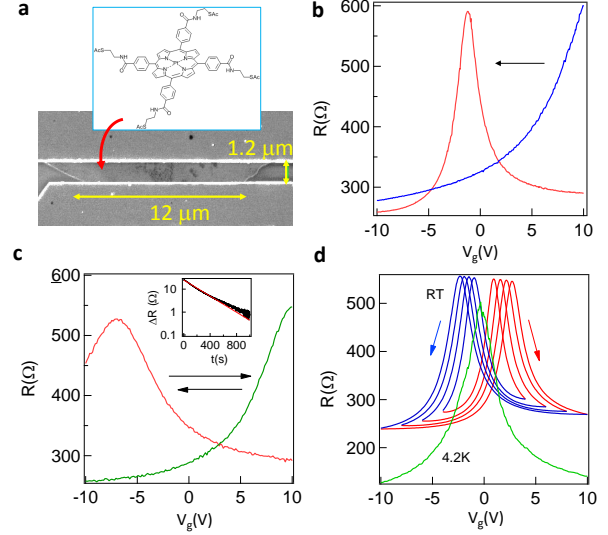


FIG. 1: Effect of Pt-porphyrin grafting at room temperature. a: Electron microscope image of the investigated graphene sample connected to Pd/Nb electrodes, and representation of the Pt-porphyrin. b: Room temperature resistance as a function of gate voltage before and after deposition of the Pt-porphyrins (blue and red curves, respectively). c: Modification of the Dirac point position after keeping the sample for one hour at $V_g = \pm 10$ V. Inset: Time evolution of the sample resistance at fixed gate voltage after a rapid gate shift from -10 to +10 V . The slow relaxation can be fitted by $\Delta R = R_0 \exp(-t/t_0)$ with $R_0 = 165$ $\Omega$ and $t_0 = 187$ $s$. d: top curves, room temperature gate variations of the two-wire resistance for different gate voltage ramps with grafted porphyrins: the hysteresis increases with gate bias amplitude. Lower curve, gate voltage variation of two-wire resistance at 4.2 K. The hysteresis disappears at low temperature. The resistance decrease of 110 $\Omega$ at low temperature is due to the transition to the superconducting state of the Pd/Nb electrodes.

electrons are transferred from porphyrins to graphene. Such a doping effect has been reported for porphyrin-grafted carbon nanotubes [8, 9] and, more recently, for Zn-porphyrins grafted graphene [10]. Second, the gate dependence of the resistance is hysteretic, with a corresponding slow exponential relaxation of the sample's resistance in response to a fast gate voltage change (Fig.

1b). Interestingly, the sign of this hysteresis is opposite to that of graphene field effect transistors with charge traps in the $SiO_2$ gate insulator [11, 12], as well as that of graphene covered with organic surfactants [13]. We relate the present hysteresis and slow relaxation to hopping processes through neighboring molecules [14, 15], leading to a slow (hundred second time scale) charge transfer through neighboring porphyrin layers above the graphene. In contrast, we believe that a much faster charge transfer occurs between the graphene and the porphyrin molecules directly in contact with graphene. Fig. 1c illustrates how keeping the sample at a non-zero gate voltage $V_g^0$ leads, at room temperature, to shifting the Dirac point to $-V_g^0$, with a broadened gate dependence of the resistance, implying induced charge inhomogeneities. We find that cooling the sample under non zero gate voltage leads to a non zero-voltage Dirac peak at low temperature. But cooling the sample under zero gate voltage leads to a Dirac peak at 0.5 V at low temperature, with no hysteresis or change. We find that the gate voltage dependence of this porphyrin-covered graphene's resistance, cooled under $V_g = 0\,V$, is nearly the same at 4.2 K and at room temperature, even though the hysteresis has disappeared (Fig. 1d). Interestingly, this dependence is much sharper after porphyrin deposition, with a higher resistance at the charge neutrality point (Dirac point) (see in Fig. 2a the comparison at 4.2 K), implying that coating with Pt-porphyrins results in a higher sample quality (when the Dirac point is near $V_g = 0$). The same consequences of Porphyrin deposition were measured on a second sample with non superconducting Pd contacts, at room temperature and 4.2 K.

Two different physical phenomena could explain these observations:(i) A fast induced charge transfer from the porphyrins to graphene that would follow the gate voltage sweep; or (ii) a decrease of the disorder scattering potential due to the neutralisation of negatively charged impurities by the positively ionised porphyrins.

We now show that the low temperature, high magnetic field experiments can discriminate between these two effects. Indeed, as shown in Fig. 2b, the position of the quantum Hall plateaux is practically unchanged after Pt-porphyrin deposition, and corresponds to the expected filling factors for monolayer graphene $\nu_n = n_c(V_g)\Phi_0/B = 4(n+1/2)$ where the carrier density $n_c$ is related to the gate voltage by $CV_g/e$, and where we have used as $C$ the capacitance per unit surface between the graphene layer and the back gate. This indicates that at low temperature the gate voltage induces no additional charge transfer to graphene (which possibly would come from the porphyrins) than in the case of the uncoated graphene. Notice how although the plateaux position is unaffected by coating, the plateaux themselves are much better defined, consistent with an improved mobility of the coated graphene. These observations suggest that the deposited porphyrins tend to neutralise the charged
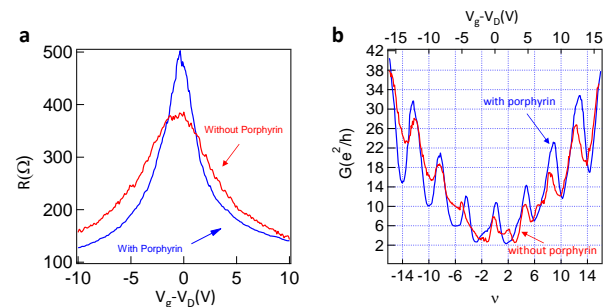


FIG. 2: Improvement of the sample quality after porphyrin grafting. a: Zero magnetic field gate-voltage sweep of two wire resistance at 4.2 K, before (red) and after (blue) deposition of the Pt-porphyrins. The origin is taken at the Dirac point $V_D$ for both curves. The sharper curve with a higher Dirac peaks demonstrates that the sample quality has improved thanks to porphyrin coating, with a mobility increase of 20%. b: Quantum Hall regime at 100 mK and in a perpendicular magnetic field of $B = 5\,T$ (for which the Nb electrodes are non superconducting), before (red curve) and after (blue curve) grafting. The gate voltage is expressed in terms of the filling factor $\nu = n_c\Phi_0/B$, with the charge density $n_c$ computed assuming that only the backgate charges the graphene. The Hall plateaux are better defined, confirming the higher sample quality. The gate voltage position of the plateaux is unchanged, demonstrating that the charge transfer between porphyrins and graphene is gate independent, and fixed at low temperature.

scattering centers on the graphene surface, leading to a reduced scattering potential and an increased mobility (from $\mu = 8\,000$ to $10\,000$ $cm^2V^{-1}s^{-1}$ near the Dirac point, at $n_c = 1.6\,10^{15}$ $m^{-2}$, corresponding to $V_g = -2.5\,V$, see Fig. 2a).

We now turn to the low temperature data obtained after cooling the sample at zero gate voltage. Fig. 3. compares the evolution of the differential resistance with gate voltage, around 100 mK, before and after deposition of the porphyrins. Before deposition, the graphene junction has zero differential resistance at low dc current, in highly doped regions (away from the Dirac point), both for hole and electron doping (Fig. 3a): this is the signature of a Josephson effect, a supercurrent running through the graphene because of the superconducting contacts. We previously reported that the amplitude of the maximal supercurrent, defined as the junction's critical current, is strongly depressed in the region of the Dirac point. We attribute this effect to specular reflections of the Andreev pairs on very low carrier density regions (puddles) where the local Fermi energy is lower than the proximity induced superconducting gap (see ref. [6] for a detailed discussion of these findings). It is clear that at high doping ($V_g > 20\,V$) the supercurrent exists for both electron and hole doping, as also shown in fig 3c. In stark contrast to this *bipolar* Josephson effect through pristine graphene (Fig. 3a and 3c), we find that after deposition of the
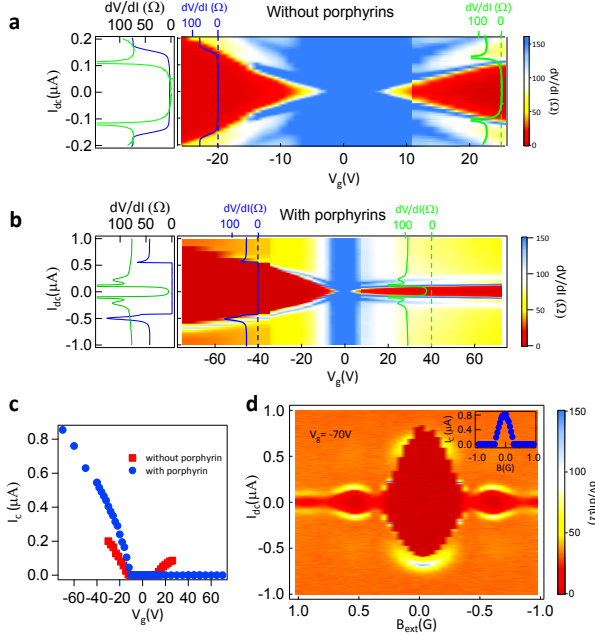
FIG. 3: Change from bipolar to unipolar induced superconductivity upon deposition of Pt-porphyrin. Colour-coded differential resistance as a function of dc current (x axis) and gate voltage (y axis), measured with a small ac current added to the dc current. The dark red regions correspond to regions of zero differential resistance where a Josephson supercurrent runs through the S/graphene/S junction. Whereas the Josephson effect occurs symmetrically on both sides of the Dirac point on the pristine, uncoated sample (a, T=200 mK), it only occurs on the hole doped side (negative $V_g$) on the sample covered with porphyrins (b, T=100 mK). The curves on and to the left of the color plots are the differential resistance curves as a function of dc current, measured at gate voltages symmetric with respect to the Dirac point. c: The change form bipolarity to unipolarity revealed by the variations with gate voltage of the critical current, i.e. highest dc current for which the differential resistance is zero, extracted from panels a and b. Before (red squares, bipolar) and after (blue circles, unipolar) porphyrin deposition. d: Differential resistance as a function of dc current and external magnetic field (applied perpendicular to the graphene sheet), for the graphene with porphyrin molecules, at $V_g = -70$ V. It is clear that a field as small as a fraction of a Gauss can suppress the induced supercurrent through graphene, because of destructive interference between Andreev pairs diffusing across the graphene. This explains how the porphyrin's magnetic spins, if they lead to magnetic domains at positive gate voltage, can create an inhomogeneous magnetic flux sufficient to destroy the proximity effect, thereby leading to a unipolar supercurrent.

porphyrin molecules, the Josephson current is enhanced in the hole doped region but suppressed in the electron-doped region. Only a dip in the differential resistance is visible at low current bias and high positive gate voltage, but no strictly zero resistance (Fig. 3b). Fig. 3c, which displays the critical current amplitude as a function of

gate voltage, shows how porphyrin deposition turns the behavior from bipolar to unipolar.

Correlatively to the strong electron-hole asymmetry of the Josephson effect, we also find an electron-hole asymmetry in the magnetoresistance (with magnetic field perpendicular to the graphene plane), presented in Fig. 4. As seen in Fig. 4b and 4d, the low temperature magnetoresistance is hysteretic at positive gate voltage (electron doping). This hysteresis decreases with increasing temperature and disappears above 6 K. In contrast, Fig. 4a and 4c show that the hysteresis is at least an order of magnitude smaller at negative gate voltage (hole doping) [17].

As is discussed below, we attribute the doping-dependent hysteresis in magnetic field and the doping-dependent suppression of Josephson current, to the magnetism of the ionised porphyrin molecules. The absence of magnetic hysteresis and the large Josephson current in the hole doped region indicate either a quenched magnetic moment for the porphyrins or a reduced exchange interaction between porphyrin's localised spins and the graphene holes, compared to electrons. Moreover the magnetic hysteresis in the hole doped region points to the formation of a magnetic order of the molecular spins, with partially oriented magnetic domains, generating a non uniform magnetic field that is revealed by the magnetoresistance of graphene, and explains the suppressed Josephson current for this doping. Indeed, as is shown in Fig. 3d, the induced proximity effect is extremely sensitive to magnetic flux. A fraction of a flux quantum through the graphene sheet suppresses the supercurrent, by destructive interference amongst Andreev pairs [18]. Since the average distance between ionised porphyrins is a few nanometers, our findings suggest a relatively long ranged magnetic interaction mediated by graphene's conduction electrons or holes.

The physics of magnetic impurities on graphene has led to a variety of interesting theoretical predictions specific to the band structure of graphene. Unlike metals, the exchange coupling in graphene is expected to be controlled by gating [1]. This effect has two important consequences. First, the amplitude of the magnetic moment of an individual impurity should strongly depend on gate voltage, causing a tunable Kondo effect. Depending on the relative energy of the impurity level with respect to the Dirac point, this Kondo effect could be strongly asymmetric with gate voltage [19]. Second, the long range magnetic Rudderman, Kittel, Kasuya,Yosida (RKKY) interactions mediated by the carriers should also be gate voltage dependent. Such interactions have been investigated theoretically and numerically by several groups[1, 21]. Characteristic coupling energies in the Kelvin range are predicted between spins 1/2 a few nanometers apart. The magnetic hysteresis we observe could then be explained by a spin glass type of order taking place at low temperature. It is however not straight-

forward to extrapolate the theoretical RKKY coupling between localised spins on graphene to the situation of Pt-porphyrins, where each spin is delocalised over the entire nanometer sized molecule. This eventual spin glass order of magnetic porphyrins mediated by conduction electrons is of great potential interest and motivates further investigations of different porphyrin species, including metal free porphyrins or ones carrying a magnetic atom.

In summary, we have shown that grafting Pt-porphyrins onto a mesoscopic graphene sheet leads to signatures of charge transfer, and that the deposited porphyrins tend to neutralise the charged scattering centers on the graphene surface. In addition, we have found that the Josephson current induced via superconducting electrodes is suppressed in the electron-doped region, but unaffected in the hole doped region. We attribute this suppression of the Josephson current to the formation of magnetic moments on the ionised porphyrins. This magnetism is also revealed by a sizable hysteretic magnetoresistance in the electron doped region, that is absent in the hole doped region. Both findings suggest a doping-dependent exchange coupling between the localised magnetic moments of the porphyrins and the charge carriers in graphene, that can therefore be controlled by gate voltage.

## METHODS

The graphene samples are obtained by exfoliation of high purity graphite and deposited onto an oxidised doped silicon wafer acting as a backgate. Monolayers are selected by optical microscopy followed by characterisation using Raman spectroscopy. The metallic contacts are made by electron beam lithography followed by sputtering of a Pd/Nb bilayer (7 nm Pd, 70 nm Nb). At low temperature (200 mK) these contacts induce superconductivity in graphene, with supercurrents up to 300 nA at large electron or hole doping, for a junction 1.2 $\mu m$ long and 12 $\mu m$ wide [6]. After this first series of measurements, we deposited Pt porphyrins on the same graphene sample at room temperature according to the following protocol. We first checked that deposition of the sole solvent tetrahydrofuran (THF) does not modify the gate voltage dependence of the sample's conductance. We then deposited a 10 $\mu l$ drop of a 1 mM solution of Pt porphyrins in THF. This corresponds to a few hundred layers of porphyrins covering the graphene layer after evaporation of the THF solvent.

The porphyrins were prepared as follows : PtII tetrakis (4-carboxyphenyl)-porphyrin [20](15 mg, 10.8 $\mu$ mol) was dissolved in NMP (4 ml). S-acetylcysteamine hydrochloride (13.54 mg, 86 $\mu$mol), benzotriazol-1-yl-oxytripyrrolidinophosphonium hexafluorophosphate (Py-BOP) reagent (44.7 mg, 86 $\mu$mol) and dry DIEA (30
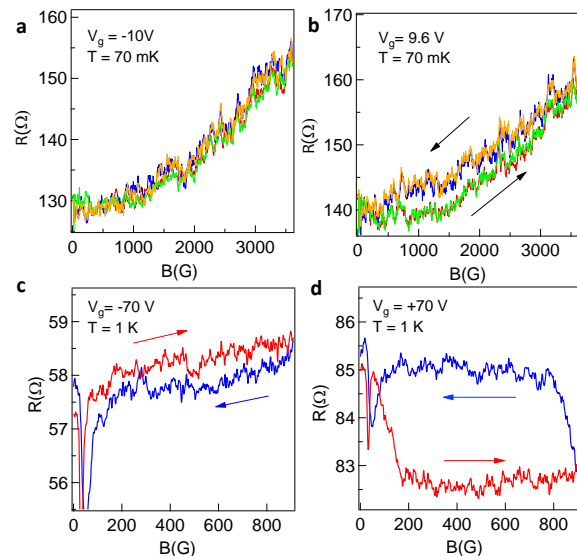


FIG. 4: Unipolar hysteresis in the graphene's magnetoresistance after porphyrin deposition, at two temperatures, with a field direction perpendicular to the graphene plane. The hysteresis is quite large at positive gate voltage (electron doping, b and d) and negligible (at least an order of magnitude smaller) for hole doping (a and c), confirming the existence of a magnetic order that suppresses the supercurrent for electron doping. The anomalies at very low magnetic field correspond to the superconductivity of the contacts, and exist both in the electron and hole doped regions. The reproducible fluctuations at 100 mK are mesoscopic conductance fluctuations. Interestingly, the amplitude of these fluctuations does not depend on carrier type, implying that the magnetic spins do not suppress the superconducting proximity effect via a drastic decrease of phase coherence but rather because of the magnetic flux they induce.

$\mu l$, 172 $\mu$ mol) were sequentially added and the resulting reaction mixture was stirred at room temperature for 4 h. The reaction was checked for completion by TLC ($CH_2Cl_2$/MeOH, 96:4, v/v). Thereafter, the crude was diluted with AcOEt (40 ml), washed by aq. 10 % citric acid (40 ml), aq. sat. $NaHCO_3$ (40 ml) and brine (40 ml). The organic layer was dried over $Na_2SO_4$, filtrated and evaporated to dryness. The resulting residue was purified by chromatography on a silica gel, eluent ($CH_2Cl_2$/MeOH: 100/0 to 97/3) , yielding porphyrins as a brown-orange solid (9.9 mg, 7.1 $\mu$mol, yield = 66 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.64 (s, 3H), 3.85 (t, J = 5.1 Hz, 2H), 4.16-4.19, (m, 2H), 8.09 (s, 8H), 8.15-8.23 (m, 12H), 8.70 (s, 4H). MS (MALDI-TOF) m/z = 1387.26 [M]$^+$, calculated for $C_{64}H_{56}N_8O_8S_4$ Pt: 1387.28 g/mol.

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[16] We find that the increased sensitivity of the graphene's conductance to the gate voltage after porphyrin deposition occurs both for thicknesses of 100 and 1000 porphyrin layers. This points to the predominant role of direct charge transfer between the first porphyrin layer and graphene, rather than a polarisation effect of the upper insulating porphyrin layers.

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